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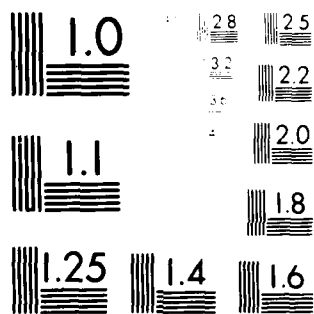
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Technical Report #26

State Selected Velocity Measurements: NO/Ru(001) Thermal Desorption

David S. King and Richard R. Cavanagh

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National Bureau of Standards  
Washington, DC 20234

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State Selected Velocity Measurements:

NO/Ru(001) Thermal Desorption

by

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ABSTRACT

> The tangential velocity distribution of ground state NO ( $J'' = 9\ 1/2$ ,  $E_{\text{rot}} = 165\ \text{cm}^{-1}$ ) thermally desorbed from Ru(001) under ultra-high vacuum conditions was measured by laser excited fluorescence Doppler spectroscopy. The measured Doppler profile was Gaussian in nature, characterized by a temperature  $T = 235 \pm 45\ \text{K}$  significantly lower than the surface temperature at the desorption peak of 455 K.



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Quantum-state specific studies of the interactions of molecules with clean, well-characterized metal surfaces are quite sparse. Molecular beam scattering has been utilized to examine angular and velocity distributions of translationally-inelastic scattered particles.<sup>1</sup> Very recently, laser excited fluorescence (LEF) techniques have been applied to the measurement of the change in rotational state<sup>2</sup> and rotational alignment<sup>3</sup> for molecular beam scattering of NO from Ag(111), the rotational distribution of NO thermally desorbed from Ru(001)<sup>4</sup>, and Doppler profiles of sputtered atoms<sup>5</sup>. To date there have been no rotational state specific measurements of translational energy for either inelastic beam/surface scattering or thermal desorption.

We report here the first measurement of a rotational-state specific velocity distribution for thermally desorbed molecules from a single crystal metal under ultra-high vacuum (UHV) conditions. The experiment is based on the measurement of a molecular Doppler profile using LEF techniques<sup>6</sup>. The absorption frequency  $\nu$  for a molecule moving with a velocity  $\vec{v}$  relative to the propagation direction of the exciting laser  $\vec{n}$  (unit) be shifted in frequency:  $\nu = \nu_0(1 + \vec{v} \cdot \vec{n}/c)$ , where  $c$  is the speed of light. Under the conditions of thermal equilibrium, a Maxwell-Boltzmann distribution of velocities and their corresponding Doppler shifts give rise to the Gaussian line-shape function:

$$S_d(\nu, \nu_0) = S_0 \exp\left[-(\ln 2) \left(\frac{\nu - \nu_0}{(\Delta\nu)_d}\right)^2\right] \quad (1)$$

Given such an equilibrium distribution, the Doppler width (FWHM)  $2(\Delta\nu)_d$  is only dependent on the translation temperature.

The sample chamber used in this work was a stainless steel UHV apparatus equipped with an ion pump, titanium sublimators, effusive molecular beam doser, and quadrupole mass spectrometer<sup>4</sup>. All experimental results reported here were obtained following saturation NO coverage of the freshly cleaned and cooled (273 K) Ru crystal and using a  $12 \text{ K sec}^{-1}$  heating rate.

The molecularly desorbed NO was probed by exciting the origin of the lowest lying  $\tilde{A}^2 \Sigma^+ \rightarrow \tilde{X}^2 \Pi_{1/2}$  electronic transition<sup>7</sup>. The ultraviolet probe laser beam was collimated with a beam area of  $0.1 \text{ cm}^2$ . In the UHV chamber the probe beam passed parallel to the  $0.7 \times 0.7 \text{ cm}$  crystal face at a distance of about 0.5 cm. After traversing the UHV chamber, the laser passed through a reference cell and into an absolute energy meter. The spectral bandwidth of the visible dye laser fundamental was measured to be  $\leq 0.015 \text{ cm}^{-1}$ . We estimate the bandwidth of the frequency doubled probe to be  $\sim 0.02 \text{ cm}^{-1}$ . The probe laser energy of 10  $\mu\text{Joule}$  in a 10 nsec duration pulse was well below the NO saturation requirement of  $1 \text{ mJoule/cm}^2$ . The accuracy of the Doppler measurements was determined by observing single NO ro-vibronic line profiles in the reference cell. The room temperature Doppler width for NO is  $2(\Delta\nu)_D = 0.086 \text{ cm}^{-1}$ ; the line profiles obtained for a  $46 \times 10^{-6}$  mixture of NO in nitrogen at an NO density of  $10^{11} \text{ cm}^{-3}$  was Gaussian between the  $e^{-2}$  points with a measured FWHM of  $0.088 \pm 0.004 \text{ cm}^{-1}$ .

In these thermal desorption experiments, evolution of NO into the gas phase only occurs during a four second interval as the crystal

temperature linearly increases from 435 - 475 K. Thus, only a single frequency component of the full Doppler profile for any individual ro-vibronic transition could be measured during an individual desorption flash. As the Ru crystal was being cycled through the annealing/dosing procedure the laser frequency was tuned to measure a new velocity component within the same ro-vibronic band. The reference cell LEF was always recorded simultaneously for normalization purposes and to provide an independent verification of  $\nu_0$ . The recovered ratioed signal is:

$$I_{J''}(\nu) = \frac{TPD_{N_{J''}}(\nu)}{ref_{N_{J''}}(\nu)} \times C^{-1} \quad , \quad (2)$$

where  $TPD_{N_{J''}}(\nu)$  represents the number density of thermally desorbed species in rotational state  $J''$  with the appropriate parallel velocity component to absorb at the Doppler shifted frequency  $\nu$ , and  $C$  is the relative detection efficiency of the two optical systems.  $ref_{N_{J''}}(\nu)$  is a Maxwell-Boltzmann distribution with a temperature of  $293 \pm 2$  K.  $TPD_{N_{J''}}(\nu)$ , which has never been previously characterized, is obtained from eqns. (1) and (2). In the figure, the thermal desorption tangential Doppler line shape for NO molecules with  $165 \text{ cm}^{-1}$  of rotational energy ( $J'' = 9 \frac{1}{2}$ ) is plotted. The data represent the average and standard deviations of 5-8 individual flash desorption measurements with peak NO ( $J''=9 \frac{1}{2}$ ) densities on the order of  $10^6 \text{ cm}^{-3}$ . The error bars reflect the reproducibility of the thermal desorption experiments, random shot noise and laser scatter, and slight frequency jitter of the probe laser

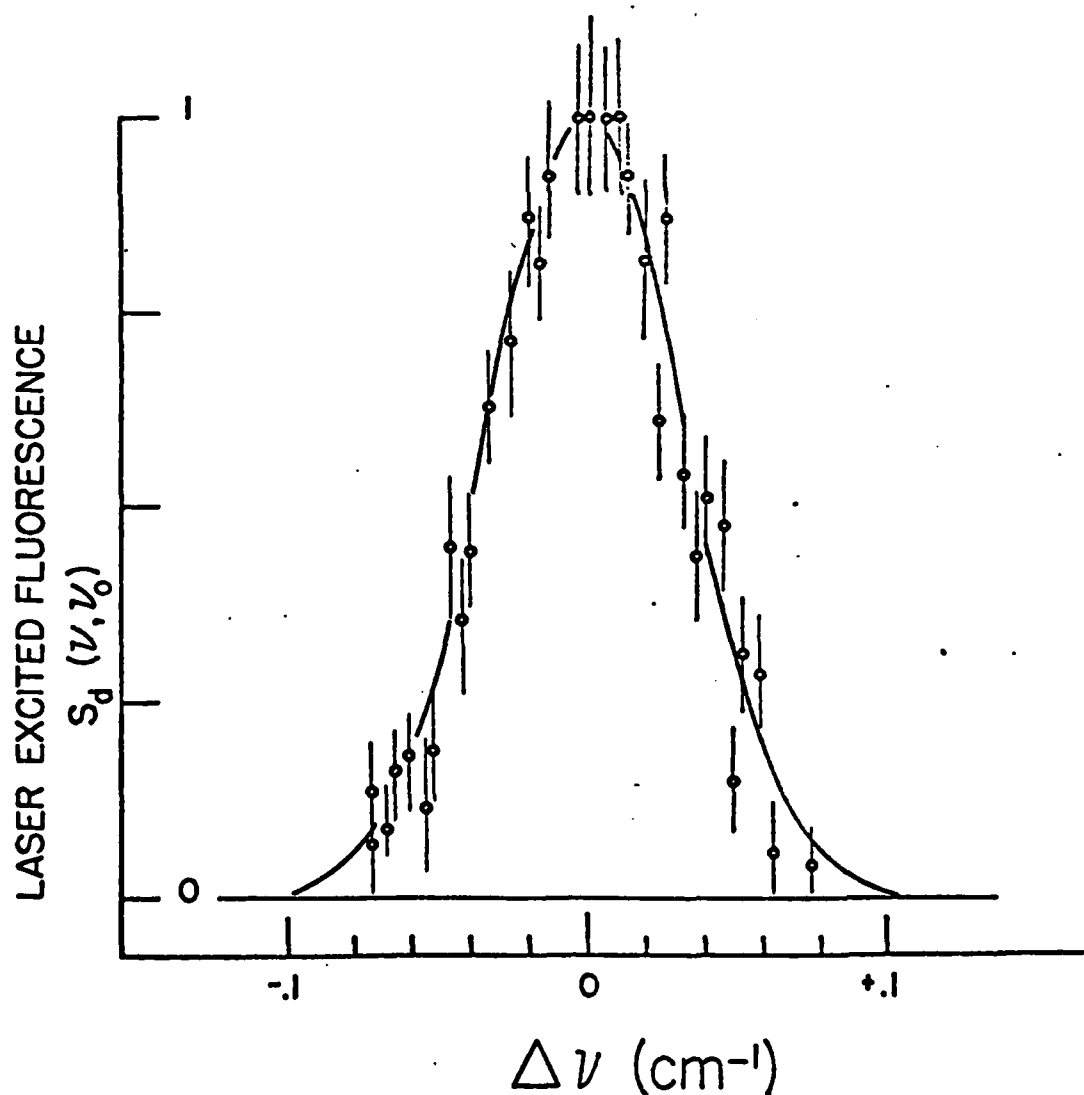


frequency. The solid curve represents the Gaussian line profile determined to give the best least squares fit to the experimental data. The data fall symmetrically about  $v_0$  and correspond to a tangential translational temperature of  $T_{//}(E_{\text{rot}}=165 \text{ cm}^{-1}) = 235 \pm 45 \text{ K}$  (at the 95% confidence level).

The important result of this work is that the tangential Doppler profile of ground state NO molecules in the  $J''=9 \ 1/2$  rotational level thermally desorbed from Ru(001) is characterized by a translational temperature significantly lower than the surface temperature of 455 K. One aspect of thermal desorption predicted by statistical theories, such as transition state theory, is full equilibration of the tangential velocity with the surface<sup>8</sup>. This is clearly not obtained in the NO/Ru(001) system. Similar effects have been observed in the gas phase where the partitioning of excess reaction energy over internal degrees of freedom and relative translational energy need not reflect the transition state but rather may arise from exit channel effects<sup>9</sup>. Whether the deviation from statistical behavior observed for NO/Ru(001) is an exit channel effect or represents a dynamical bias<sup>10</sup> in the thermal desorption process is, at this early point, unknown. We are currently measuring the dependence of  $T_{//}$  on rotational state and the angular distribution of desorbing species. The results of these studies will be presented in a full manuscript including further experimental detail.

This work supported, in part, by a grant from the Office of Naval Research.

FIGURE CAPTION: Laser Doppler profile of NO ( $J''=9\ 1/2$ ,  $E_{\text{rot}}=165\text{ cm}^{-1}$ ) thermally desorbed from Ru(001) as measured parallel to the crystal face. The crystal temperature at the thermal desorption maximum was 455 K. The laser bandwidth was  $0.02\text{ cm}^{-1}$  and the zero Doppler shift frequency was  $44,252\text{ cm}^{-1}$ . Least squares fitting to a Gaussian line profile gave a tangential velocity distribution characterized by the temperature  $T_{//}(J''=9\ 1/2)=235 \pm 45\text{ K}$ .



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